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ANNUAL INTERIM REPORT

CHEMICAL INITIATION OF FAE CLOUDS

SUBMITTED TO:

Department of the Air Force  
Office of Scientific Research  
Directorate of Aerospace Sciences  
Bolling AFB, Washington, D. C. 20332

Attention: Dr. Bernard T. Wolfson

Under Contract No. ~~XXXXXXXXXX~~

F49620-77-C-0097

Submitted by:

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ARC No. 47-5711

November 1979

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Technical Information Officer

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# ABSTRACT

Laboratory experiments with liquid fuel and  $\text{ClF}_3$ (CTF) or  $\text{BrF}_3$  (BTF) have suggested that an effective FAE blast may be obtained by very rapid fuel/agent dispersion and agent-induced combustion. In the current work, initial small-scale field tests using small pellets of high-explosive for fuel and agent dispersion have yielded significant FAE blasts when performed in open air, no blast when performed in an atmosphere of nitrogen, and a very strong blast when performed in an atmosphere of oxygen. The results show that an agent such as CTF meets the requirements of inducing very rapid combustion, and that the strength of the FAE blast is thus principally governed by the size and configuration of the central dispersing charge. Further small-scale tests are scheduled in which the central charge is substantially enlarged and shaped for injecting high velocity jets of fuel/agent dispersion into the surrounding atmosphere.

The workshop discussions on January 25, 1979, have produced a mutual understanding of the different approaches to the FAE III problem by the various groups of investigators. A concise summary has been prepared by Moen (1). In particular, the work at McGill University is principally directed toward means of obtaining a time sequence of energy release which produces coherent pressure pulses for shock wave amplification to detonation - the SWACER mechanism. Practical considerations of FAE systems dictate that these studies should be performed with hydrocarbon fuels, but there are no constraints on the selection of candidate chemical agents for generating the free-radical concentration required by explosive fuel/air reactions. In this respect the workshop has produced various suggestions which invite reaction-kinetic studies. On the other hand, the studies at Atlantic Research Corporation are based entirely on the use of the interhalogens  $\text{ClF}_3$  (CTF) and  $\text{BrF}_3$  (BTF), whose handling and chemical-kinetic performance have become increasingly familiar in the course of laboratory studies and small-scale field tests. The experience that has been obtained with these agents suggests the possibility of obtaining simultaneous fuel dispersion and combustion at such high rate that an effective blast-generating piston force is maintained throughout the process of cloud generation and combustion. That is, it is thought to be possible to obtain an effective FAE blast by mass flow generated by very rapid fuel dispersion and combustion. This concept bypasses the SWACER mechanism and at this time continues to be the central theme of test planning at Atlantic Research. However, it is by no means ruled out that the expected accumulation of test experience and increased understanding of fuel and agent performance will in time permit a fusion of the principles of blast generation by mass flow and coherent energy release in an effective FAE III system. In order to assist the development of experimental programs in this direction, the results of previous work on the reaction kinetics of hydrocarbon/oxygen/fluorine-agent systems have been collected and reorganized in summary form. This paper is included in Moen's report on the workshop discussion, and is appended to the present report.



## 2.0 WORK DONE DURING THE REPORT PERIOD

### 2.1 Apparatus and Experimental Procedure in Small-Scale Tests with CTF and BTF

The test concept was based on the consideration that energetic but manageable agents such as CTF and BTF can be used in the dual role of promoting the fuel dispersion and initiating the explosive reaction between the dispersed fuel and the entrained air. The feasibility of this concept was originally suggested by laboratory experiments and has been further explored in the present outdoor tests.

As shown in Figure 2.1, an annular stainless-steel vessel containing about 32 cc of the agent is surrounded by 350 cc of liquid fuel and ruptured by the detonation of a central pellet of 3.3 gram RDX. Initial confinement is provided by two massive cylindrical steel blocks. A #8 detonator is rigidly mounted in the upper block with a clearance of 0.02 in. from the RDX-pellet. CTF is admitted to the agent vessel as a vapor and condensed to liquid by cooling the vessel with dry ice. BTF is a liquid with low vapor pressure at room temperature and is thus directly metered into the vessel. The vessel valves are closed and the agent quantity is determined from the weight of the vessel before and after the agent has been admitted.

The agent vessel is placed in a groove in the lower steel block and the RDX pellet is inserted. The upper block is put in place and rests on the mechanically strong agent vessel, leaving a 3/4 in. space between the two blocks. The space is closed at its circumference by plastic tape, and diesel oil or heptane is admitted through holes in the upper block. This is done by remote control and subsequently the electric detonator circuit is readied for firing. In case of a misfire, which has not occurred in these tests, it would have been possible to disarm the device by lifting the upper block from a safe distance by a block-and-tackle arrangement.

The diagnostics that has been used in this work comprises:

- (1) Measurement of the shock pressure by blast gages that are oriented to allow the blast wave to pass over the surface of the sensing element without impingement;

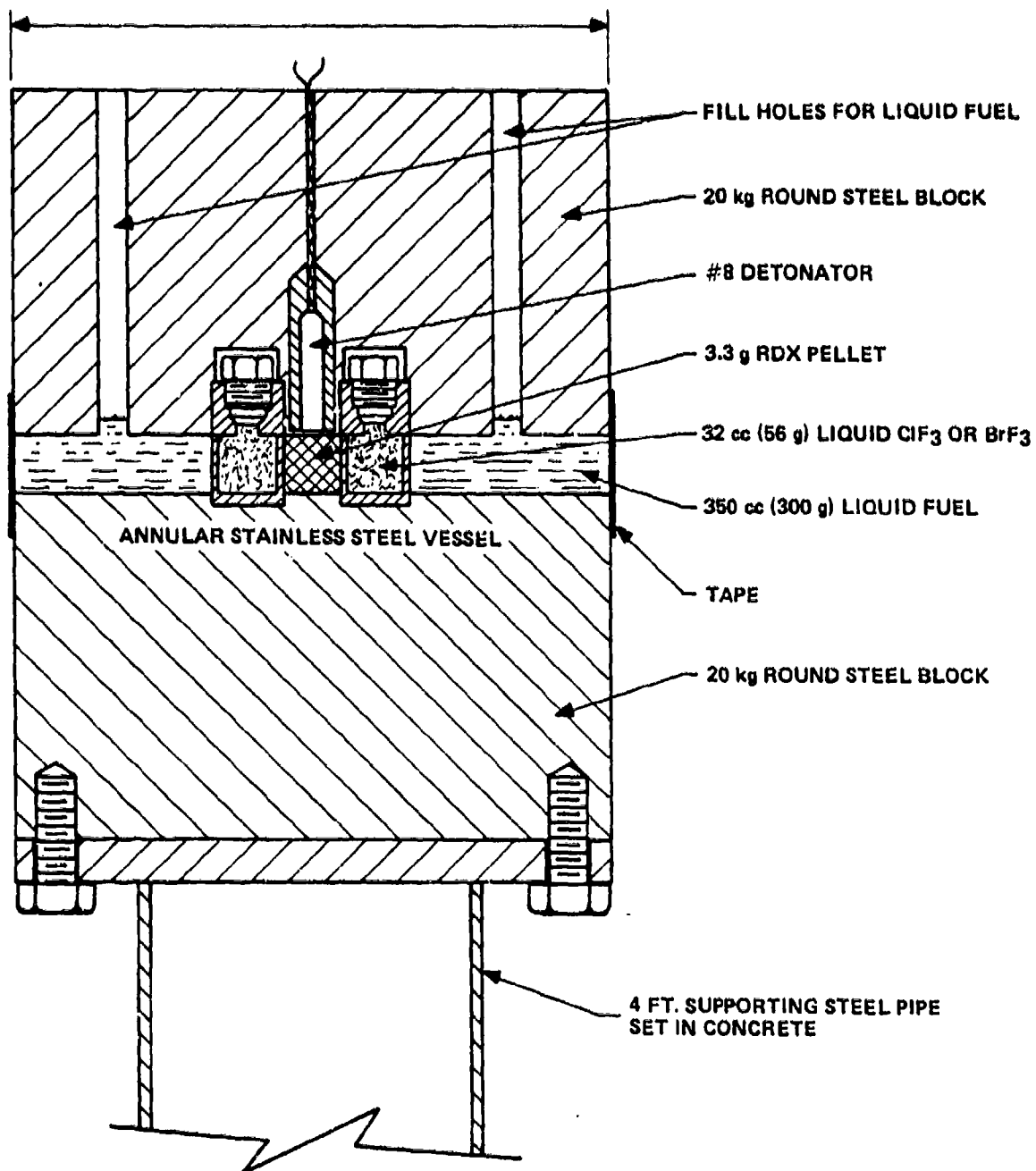


Figure 2.1. Test Bomb

(2) Measurement of the blast wave velocity by determining the time of arrival of the blast wave at gages placed at various distances from the test bomb; and

(3) High speed motion pictures of the propagation of the luminous flame zone behind the blast wave.

Figure 2.2 shows the disposition of the blast gages in open air tests with CTF and BTF. Figure 2.3 shows the test arrangements in experiments with nitrogen and oxygen atmospheres. Nitrogen was contained in a plastic-sheet tent which permitted unobstructed blast gages to be placed up to a distance of six feet from the test bomb. The oxygen requirement of the fuel is sufficiently small to be accommodated by a rather small tent, as shown. This tent had an opening to allow an unobstructed path of the blast wave to the nearest blast gage at three feet distance, thus avoiding the impingement of tent fragments on the gage. Furthermore, the test was constructed to bisect the test bomb as shown, so that one-half of the fuel cloud was passing into oxygen and the other half into the open atmosphere.

## 2.2 Test Results

Tests were performed with diesel oil and heptane. As shown by the compilation of the test data in Table 1, there were no differences in the performance of these fuels.

Figure 2.4 shows the pressure traces registered by the various blast gages in open-air detonation with CTF and Diesel oil. The zero-time signal corresponds to the closing of the electric detonator circuit. Figure 2.5 shows a plot of the shock pressure versus the distance from the bomb center in juxtaposition to a plot of the shock wave velocity calculated from the shock pressure. From these data the time of arrival of the shock wave at various distances from the bomb center is calculated on the assumption that the time delay between closing of the detonator circuit and formation of the shock front is negligible. As shown at the bottom of Figure 2.5, this assumption is validated by the agreement of the calculated and experimental times of arrival at the various blast gages.

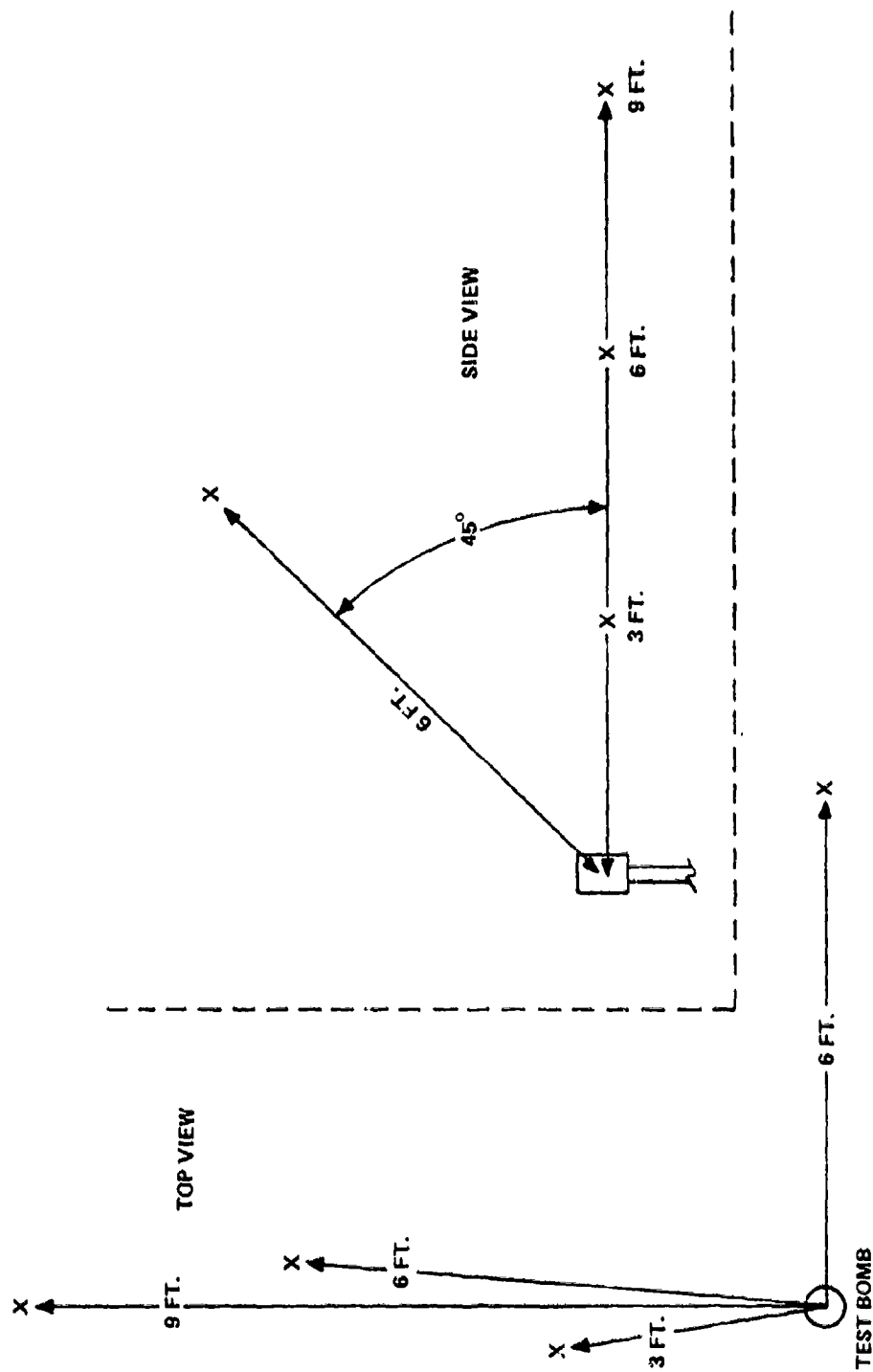


Figure 2.2 Blast Gage Positions (X)

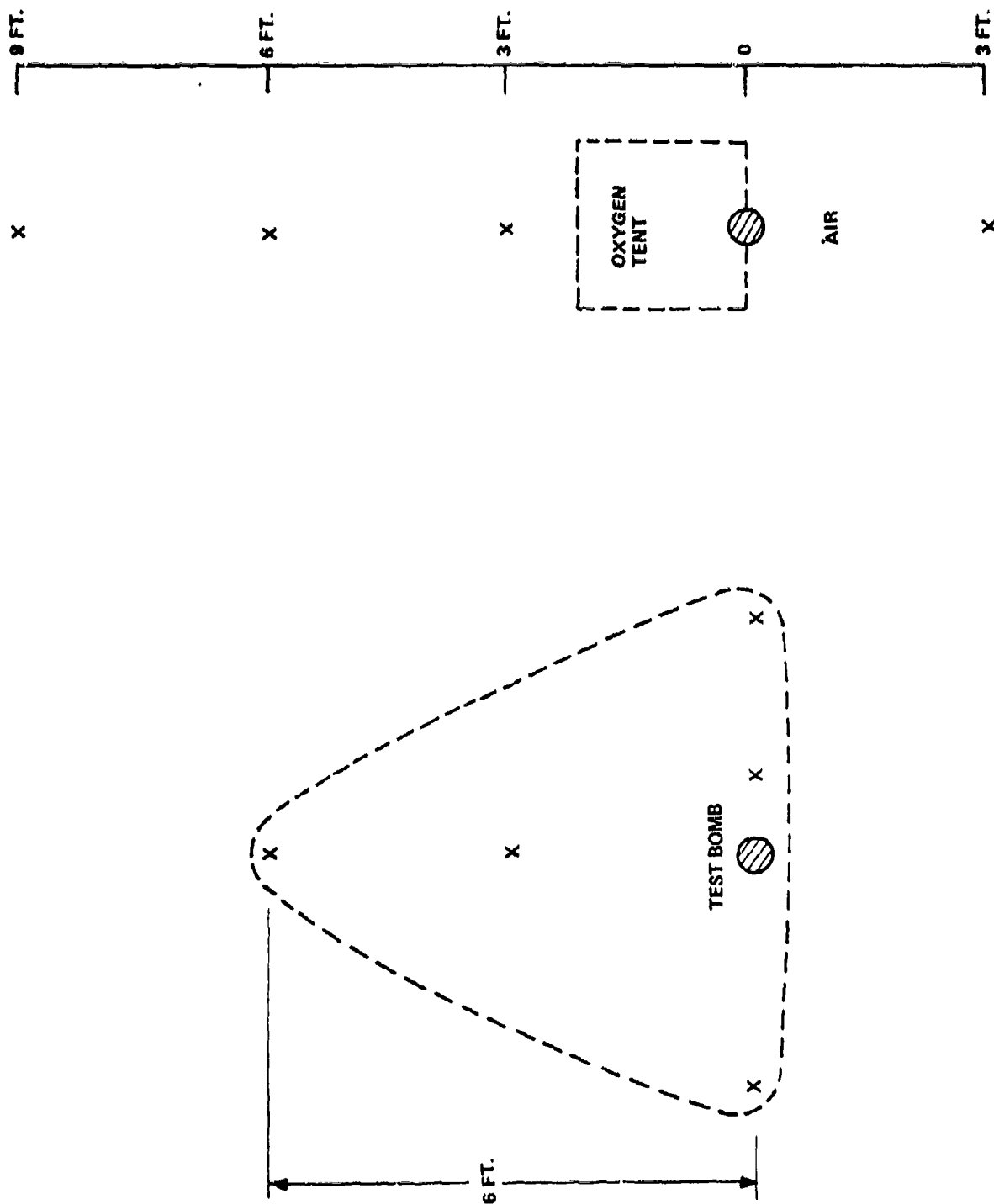


Figure 2.3 Tests in Nitrogen and Oxygen Atmospheres  
(X - Blast Gages)

TABLE 1. Summary of FAE Tests

Tests were performed in atmospheres of air, oxygen and nitrogen using 350 cm<sup>3</sup> liquid fuel, 35 cm<sup>3</sup> CTF or BTF, and a central charge of 3.35 gram RDX with a #8 detonator.

The blast gages were placed in the plane of the 3/4 in. cylindrical test configuration at 3, 6 and 9 feet from the center, and at a 45° angle to the plane at 6 feet from the center. The times of arrival of the shockwave at the stations date from the instant of detonator initiation.

Test Station	3'	6'	9'	6' (45°)
<u>CTF with Diesel oil or heptane* in air</u>				
Shock pressure, psi	14, 12.5*	6.5	4.1	2.3
Time of arrival, msec	1.7	3.9	6.3	3.9
<u>BTF with Diesel oil in air</u>				
Shock pressure, psi	16.7	3.6	(2.7 max)	3.4
Time of arrival, msec	5.3	7.4	(wave train)	7.4
<u>CTF with heptane* in O<sub>2</sub></u>				
Shock pressure, psi	73	6.3	3.1	-
Time of arrival, msec	1.5	3.5	5.9	-

CTF and N<sub>2</sub>

No shock registered by the gages (see text)

\*Split configuration, see text.

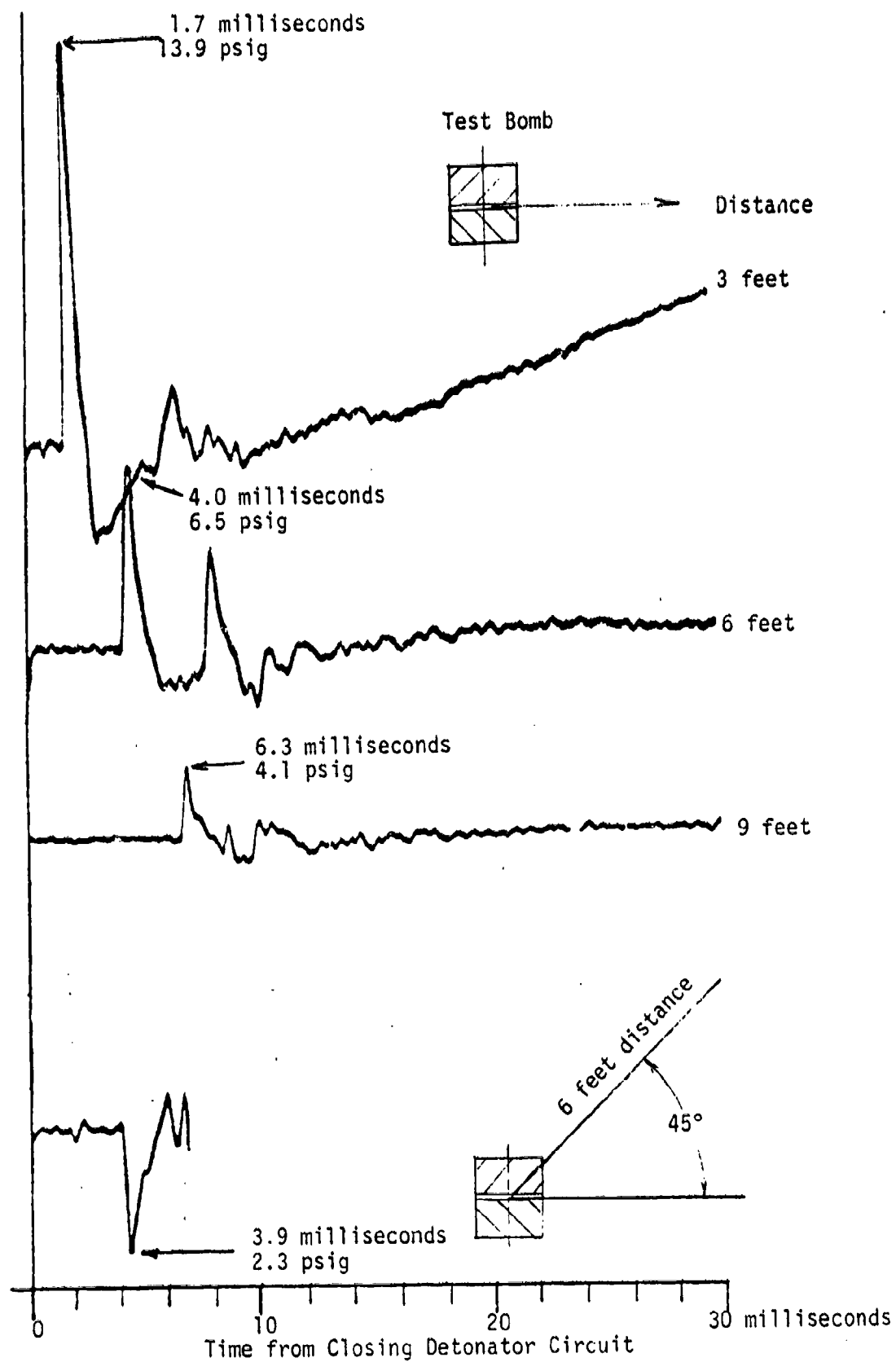


Figure 2.4 Open-Air Test with CTF and Diesel Oil

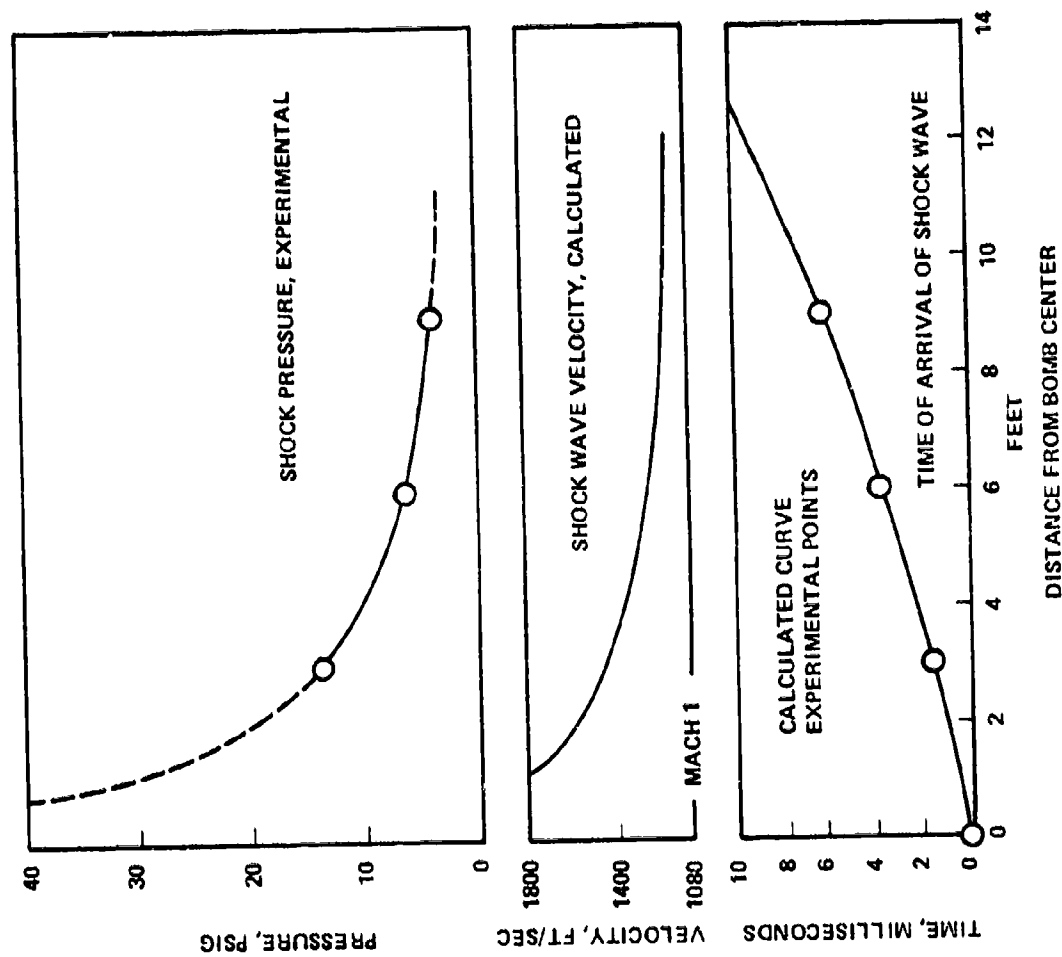


Figure 2.5. Open-Air Test with CTF and Deisel Oil



The attenuation of the shock wave by radial and lateral propagation is illustrated in Figure 2.6. In terms of Mach numbers the shock strength is rather low even in the vicinity of the test bomb which reflects a rather slow release of combustion energy behind the shock front. In corroboration, the photographic record shows that the fireball grows to a radius of several feet but that the linear rate of growth is of the order of 1/2 ft per millisecond, which is too slow for maintaining an effective piston force. However, the immediate objective was to demonstrate that the blast wave is generated by fuel/air combustion rather than by RDX detonation and explosive reaction of CTF with the hydrocarbon fuel. This has been accomplished by repeating the test in a nitrogen atmosphere, using the experimental arrangement of tent and blast gages shown in Figure 2.3. A dense cloud of fuel mist was captured by the tent, and there was no response of the blast gages until eight milliseconds after the detonator had been initiated. This delayed response is attributable to fuel/air explosion subsequent to the perforation of the tent wall near the bomb (see figure 2.3), which allowed some of the CTF-activated fuel to escape and mix with air. The lack of any prior signal from the blast gages proves that in these test the initial shock generated by the RDX detonation and the explosive CTF/fuel reaction is completely absorbed by the process of fuel dispersion, and that the blast obtained in open-air tests is thus a true FAE effect with no contribution from the initial explosive processes within the test bomb.

With CTF there were streaks of carbon deposits on the faces of the confining steel blocks, showing that the explosive CTF/fuel reaction occurs with virtually zero induction period, so that much of the CTF reacted with the fuel before the fuel was ejected from the bomb. This was not the case with BTF. As shown by the data in Table 1, with CTF the shock wave arrived at the 3-foot station at 1.7 milliseconds after detonator initiation, whereas with BTF the time was 5.3 milliseconds. A significant induction period of the BTF/fuel reaction had already been observed in previous laboratory experiments. In the present case, it proved to be sufficiently long to permit the ejection of an unreacted fuel/agent dispersion by the RDX charge and the generation of an activated FAE cloud which exploded after a time delay. The air entrainment at the end of the induction period was sufficiently large to

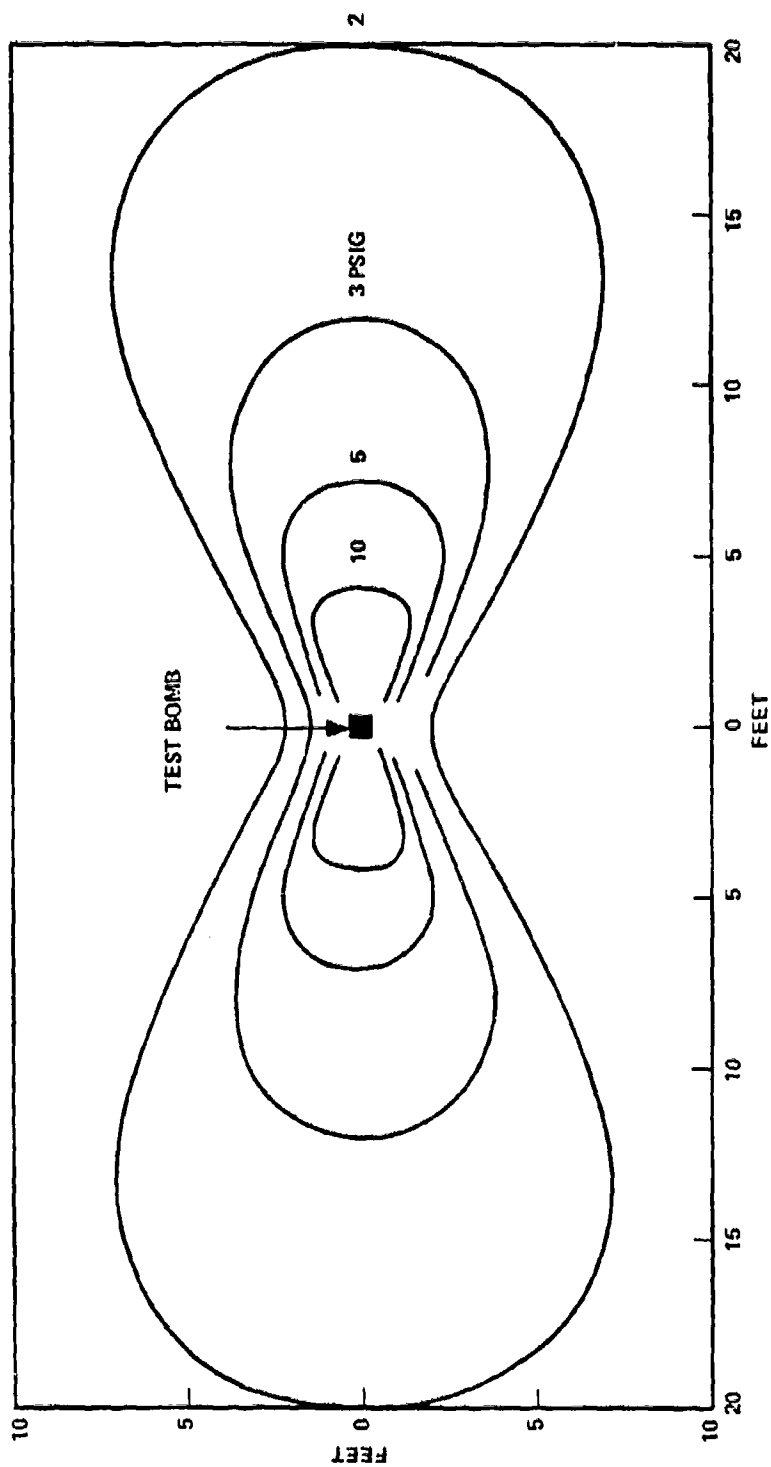


Figure 2.6. Approximate Blast Pressure Profile in Open-Air  
Test with CTF and Diesel Oil

generate an initial shock pressure considerably exceeding the shock obtained with CTF. This is shown by the curves of shock pressure versus distance in Figure 2.7. However, the curves also show that with BTF the fuel/air reaction was decelerating more rapidly than with CTF, inasmuch as the BTF-induced blast wave decays more rapidly than the CTF-induced wave. This indicates that CTF generates much higher free-radical concentrations than BTF even though the energy of the CTF/fuel reaction is completely absorbed by the process of fuel dispersion.

The rate of release of combustion energy is governed by the free-radical concentration and by the rate of entrainment of atmospheric oxygen by the cloud. It is therefore accelerated by substituting oxygen for air, which has been done by means of the tent configuration shown in Figure 2.3. As shown by the curve for CTF and  $O_2$  in Figure 2.7, the shock pressure near the test bomb is very high and probably corresponds to a shock Mach number close to 7. However, due to the small test scale the wave decays at a high rate, and the approach to sound velocity is more rapid than with CTF and air because with oxygen the fuel supply becomes rapidly exhausted.

### 2.3 Chemical Kinetics of FAE Initiation by Fluorine Agents

A paper has been prepared which summarizes the Atlantic Research work on the free-radical chain-branching reactions in systems of hydrocarbons and oxygen with  $F_2$ ,  $ClF_3$  and  $BrF_3$ . Other chemical agents are also considered, and the Atlantic Research concept of FAE III research with fluorine agents and liquid fuels is discussed. The paper is reproduced on pages 40-51 of Moen's report on the AFOSR workshop on FAE III and is included in the present report as an appendix.

### 3.0 FUTURE WORK

In small-scale tests it is not possible to maintain an effective piston force over large distances from the source, but means of improving the blast yield can be studied more efficiently if the test scale is kept small. Thus, further small-scale tests are being prepared in which emphasis is placed on very rapid ejection of the fuel and agent into the atmosphere, in order to obtain a high rate of air entrainment and high free-radical concentrations. The test concept is illustrated in Figure 3.1. The central charge of high-explosive is greatly enlarged and the shaped-charge effect is used to propel

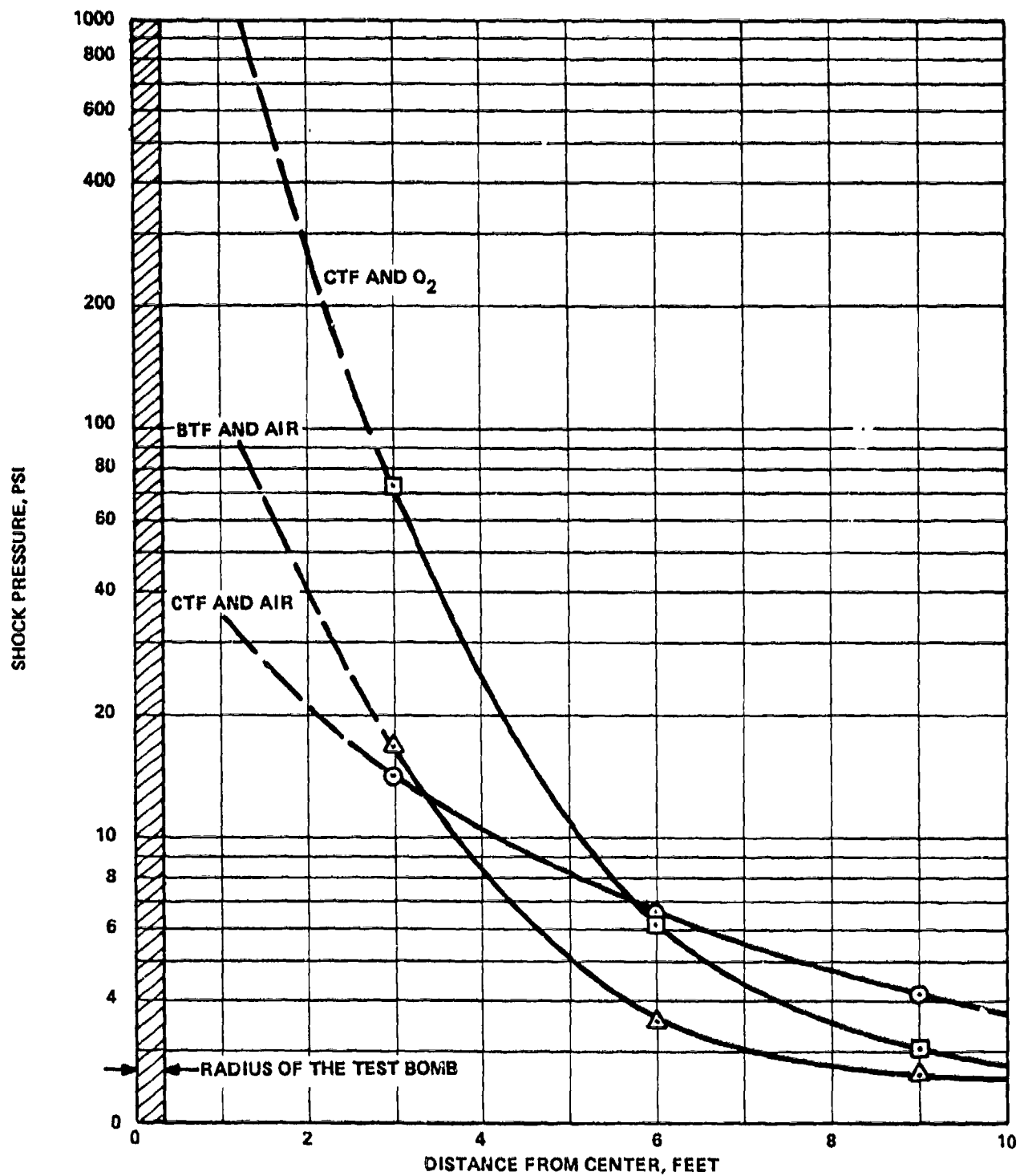


Figure 2.7 Plot of Shock Pressures in the Plane of the Test Configuration.

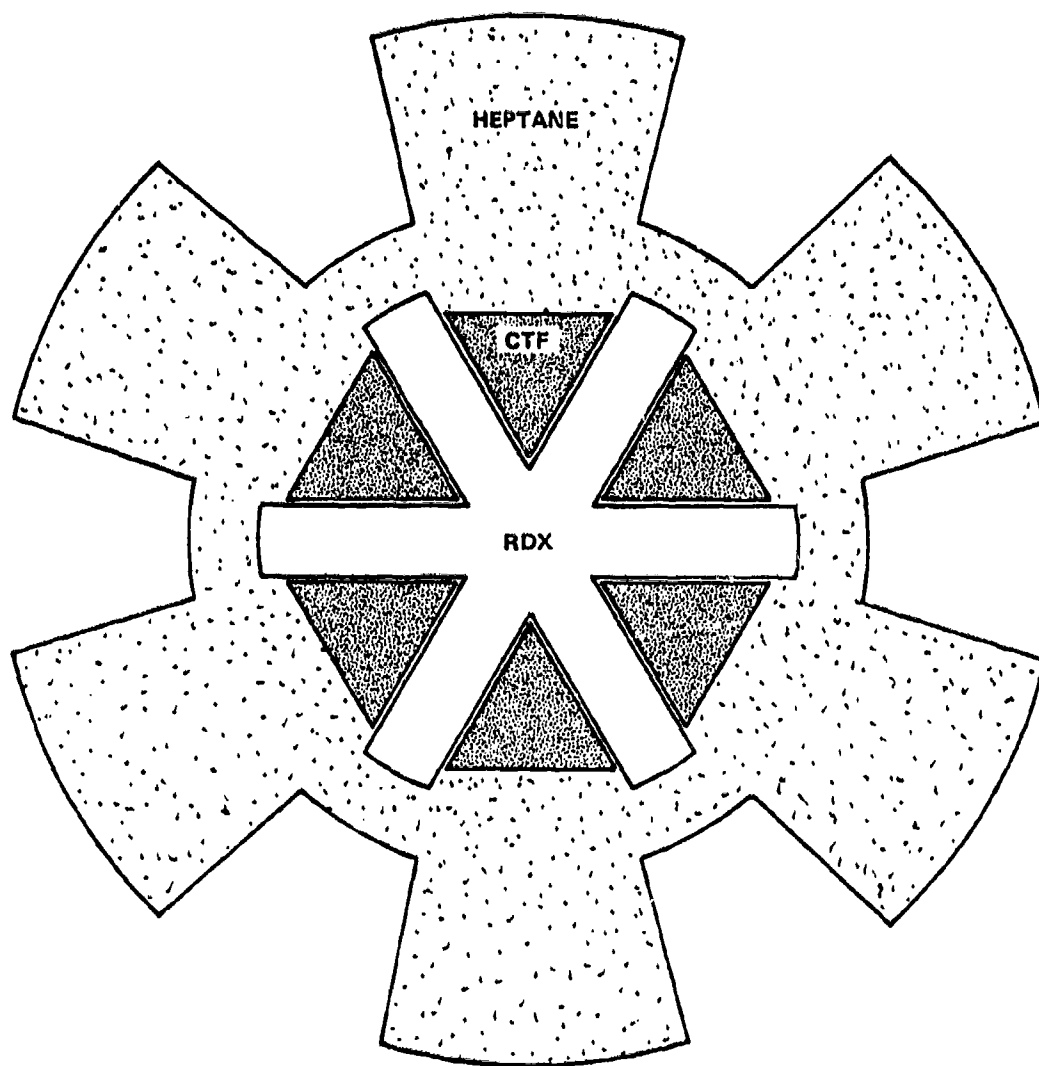


Figure 3.1. FAE Test Concept Using a Shaped Charge for Fuel and Agent Dispersion

jets of fuel and agent dispersions into the surrounding atmosphere at a high rate. It is thought that in this way a strong initial shock is generated and supported by rapid air entrainment and release of combustion energy, as illustrated conceptually in Figure 3.2. It seems probable that, in contrast to the previous test configuration, the CTF/hydrocarbon reaction plays no significant role in the process of fuel ejection from the test bomb and takes place instead mainly within the cloud, supporting the mixing process by its energy release and generating a very high free-radical concentration. In this way it should be possible to obtain much higher shock Mach numbers than in the previous tests.

It should be sufficient to use only a segment of the cylindrical configuration, as illustrated in Figure 3.3. As before, the test section will be 3/4 in. thick and will be confined between steel blocks. In case of misfire the device can be disarmed by pulling the blocks apart from a safe distance. Although the central charge is substantially larger than in previous tests, it should be noted that its energy potential plus the energy potential of the CTF/hydrocarbon reaction is still far below the energy potential of the fuel/air reaction. In compliance with a suggestion received from the sponsor, the fuel will be heptane instead of Diesel oil.

The relative contributions of the central charge of the agent/fuel reaction and of the fuel/air reaction to the blast effect will be determined by tests in open-air and in a nitrogen atmosphere, and by a blank test in which the central charge is detonated without agent and fuel. It should also be instructive to perform a test with BTF instead of CTF, as has been done previously.

#### 4.0 REFERENCES

1. Ingar O. Moen, "Report on the AFOSR Workshop on FAE III," McGill University, Department of Chemical Engineering, January, 1979.

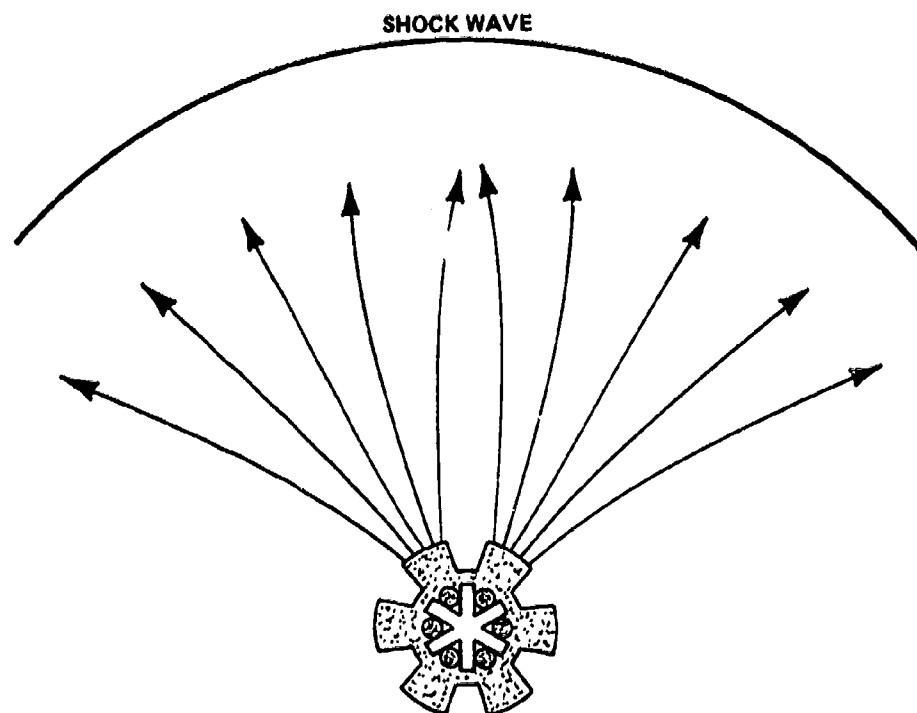


Figure 3.2. Concept of Test Performance

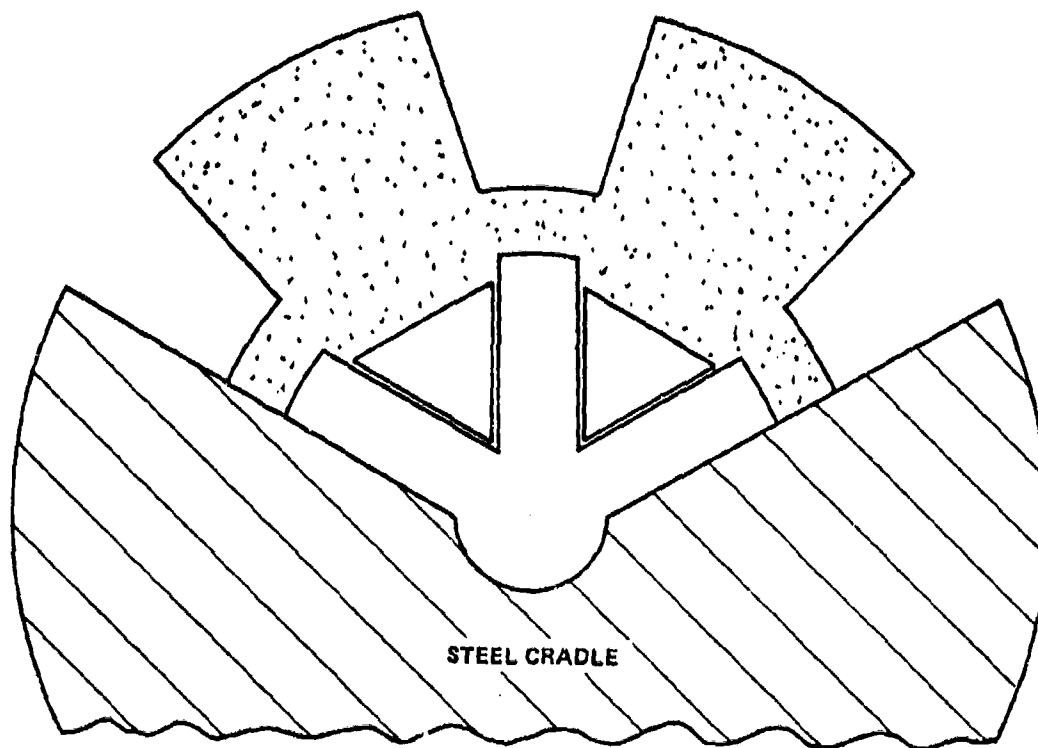


Figure 3.3. Test Section,  $\frac{3}{4}$  in. thick, 7 in. radius  
Confined Between Steel Blocks



APPENDIX A

CHEMICAL KINETICS OF FAE INITIATION

ATLANTIC RESEARCH CORPORATION CONTRIBUTION TO  
AFOSR WORKSHOP ON FAE III

(See Reference 1 of Report.)

## CHEMICAL KINETICS OF FAE INITIATION

G. von Elbe and E. T. McHale  
Atlantic Research Corporation

### INTRODUCTION

Following the AFOSR workshop on FAE we have collected the results of previous research on hydrocarbon/oxygen/fluorine-agent reaction kinetics and reorganized them in summary form. We attempt to present here pertinent results and conclusions in a way that may be helpful to others who may be engaged in planning experiments concerned with chemical initiation of pre-formed gaseous or droplet fuel-air clouds and studies of the SWACER concept. While the following discussion can provide considerable practical guidance, it will be obvious to the reader that the chemical kinetics of initiation is rather complicated and also widely different for each fuel/agent system. It is apparent that it is not possible at this time to implement the theory of the SWACER effect by Lee and coworkers with reliable chemical-kinetic data on characteristic reaction times or induction periods. It seems that this problem can only be resolved by further experimentation, but it can also be simplified to some extent. The theory introduces the time  $t_3$  which is defined as the characteristic reaction time of the catalytic agent reaction that produces free radicals; and the time  $t_4$ , defined as the induction time of the secondary main fuel-air reaction that is initiated by the free radicals. However, as discussed below, the chemical process runs continuously at a self-accelerating rate through the induction period of the agent reaction to burn-out of the fuel-air mixture. It is thus possible to combine the times  $t_3$  and  $t_4$  into a single characteristic time of the total chemical process.

### GENERAL CHEMICAL KINETICS OF FAE INITIATION

The chemical energy release proceeds via collisions of free radicals, viz., molecules carrying a free chemical bond, with neutral molecules of fuel, oxygen and intermediate reaction products. The probability of occurrence of chemical reaction in such collisions at ordinary temperatures exceeds the probability in collisions between neutral molecules by at least twenty orders of magnitude, due to the comparatively low activation energies  $E$  of the free-radical reactions and the correspondingly large Arrhenius

factors  $\exp. (-E/RT)$ . In reactions of this type the free chemical bond is transferred to one of the product molecules and may thus continue the reaction chain. The chain is broken if the product free-radical is substantially non-reactive, as for example the radical  $HO_2$ , or if two free radicals combine to form a neutral molecule. The latter process becomes significant only at the high free-radical concentrations in the final stage of the combustion process. The chain branches if the reaction is sufficiently energetic to break a chemical bond and to separate the molecular fragments, thus generating two new free radicals.

Omitting free-radical recombination reactions, the free-radical concentration  $n$  increases exponentially at the rate

$$\frac{dn}{dt} = (\alpha - \beta)n + n_0$$

where  $n_0$  is the rate of spontaneous free-radical generation and  $\alpha$  and  $\beta$  are the coefficients of the rates of chain-branching and chain-breaking, respectively. Accordingly, the time  $\tau = 1/(\alpha - \beta)$  is the characteristic time of the induction period. The coefficients  $\alpha$  and  $\beta$  are determined by the reaction mechanism, i.e., by the interlocking sequence of "elementary" reactions. They are thus functions of the reactant concentrations and the rate coefficients  $k$  of the elementary reactions. For binary reactions and unimolecular decomposition reactions the coefficients  $k$  have temperature functions of the form  $k = A \exp. (-E/RT)$ .

In common fuel-oxygen systems at ordinary temperatures  $\alpha \ll \beta$ , and  $n_0$  may be merely the rate of molecular break-up due to factors such as terrestrial radioactivity, so that such systems are stable. "Chemical" initiation of the explosive reaction is obtained with an agent that introduces a chain-branching reaction with a very low activation energy into the system. Depending on the quantity and distribution of the injected agent the resulting condition  $\alpha > \beta$  is maintained initially by the agent reaction and later by the chain-branching mechanism of the main fuel-oxygen reaction. This leads to continuous self-acceleration of the total reaction by chain branching and temperature increase until the reactants become exhausted, and the division of the process into periods  $t_3$  and  $t_4$  is eliminated.

PROPANE, BUTANE, AND HIGHER HYDROCARBONS WITH OXYGEN AND FLUORINE  $\frac{1}{2}$

Denoting the propyl radical  $C_3H_7$  by R, the chain branching and breaking reactions for propane,  $C_3H_8$ , are schematically represented by

1.  $R + O_2 = ROO$
2.  $R + F_2 \longrightarrow \text{inert radicals (chain breaking)}$
- a.  $ROO + F_2 \longrightarrow 3R \text{ (chain branching)}$
- b.  $ROO + O_2 \longrightarrow HO_2 \text{ (chain breaking)}$

This mechanism yields

$$\alpha = k_1 [O_2] \frac{2 k_a ([F_2]/[O_2])}{k_a ([F_2]/[O_2]) + k_b}$$

$$\beta = k_1 [O_2] \frac{k_b}{k_a ([F_2]/[O_2]) - k_b} + k_2 [F_2]$$

and introducing the dimensionless parameters

$$x = 2 k_1 k_a / k_2 k_b \text{ and } y = 2 (k_a \cdot k_b) ([F_2]/[O_2]) \text{ one obtains}$$

$$\alpha - \beta = k_2 [F_2] \left( x \frac{1 - 1/y}{0.5y + 1} - 1 \right) = \frac{1}{\tau}$$

In a plot of the ratio  $[F_2]/[O_2]$  versus temperature the condition  $\alpha - \beta > 0$  is found experimentally within the peninsula-shaped area marked "explosion" that is shown in Figure 1. The boundary of the area corresponds to the condition  $\alpha - \beta = 0$  which from the foregoing equation can be written in the form

$$y = (x-1) \left( 1 \pm \sqrt{1 - \frac{2x}{(x-1)^2}} \right)$$

This function is plotted in Figure 2. Introducing Arrhenius functions it is found that with  $x = 23.7 \exp. (-1280/RT)$  and  $y = 1.74 ([F_2]/[O_2]) \exp. (2520/RT)$  a perfect fit of the experimental data to the theoretical curve is obtained, as shown in Figure 2. The signs of the exponents show that reaction of the radicals with  $O_2$  have larger activation energies than reactions with  $F_2$ . The anomalously large pre-exponential factor of  $x$  points to a "steric" factor  $< 1$  in  $k_2$ , which is to be expected because collisions of R and  $F_2$  frequently yield  $RF + F$ , followed by  $RH + F = HF + R$ , which is chain-continuing and thus does not enter into the explosion mechanism.

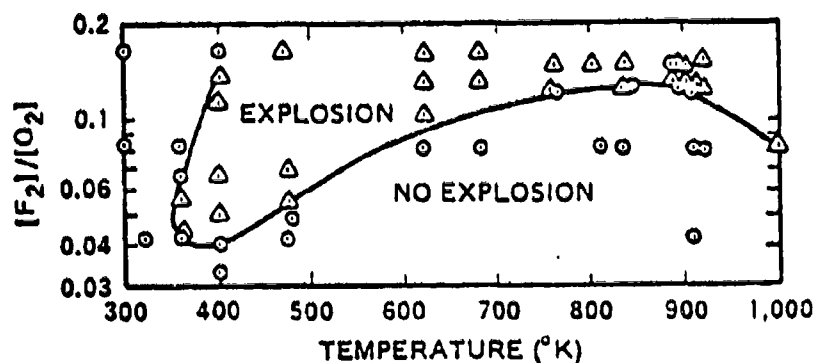


Figure 1. Explosion Limit in Propane-Oxygen-Fluorine Mixtures

Data obtained by adiabatic piston compression of argon containing low concentrations of propane and oxygen, followed by closely timed injection of a small quantity of fluorine/nitrogen mixture by means of an auxiliary piston and cylinder. The data are believed to apply to essentially homogeneous mixtures unaffected by heat loss and turbulence (Ref. 1).

Above about 600°K the chain-branching mechanism of the main propane-oxygen reaction becomes significant.

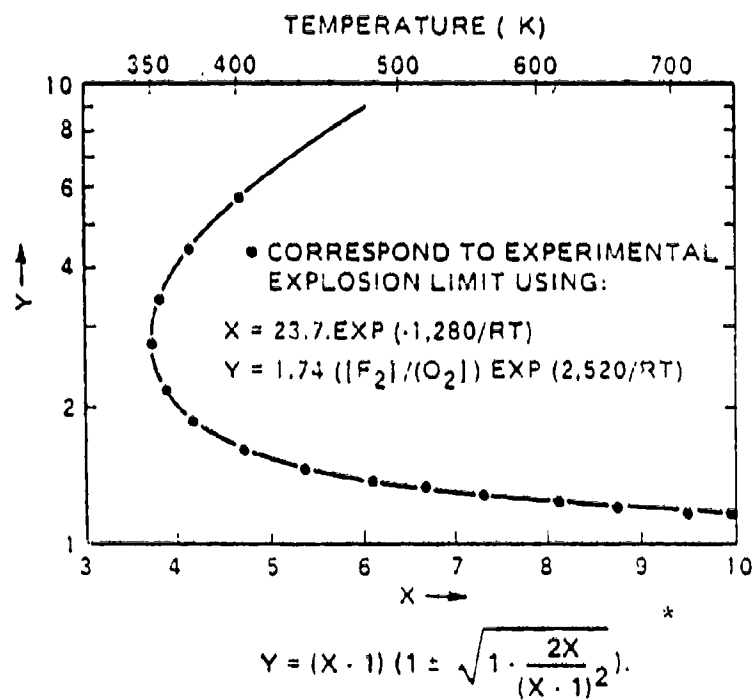


Figure 2. Curve-Fitting of the Experimental to the Theoretical Explosion Limit. (Ref.1)

Satisfactory numerical calculations of  $\tau = 1/(\alpha - \beta)$  require a better knowledge of the value of  $k_2$  than has been obtained in this work. At high  $F_2$  - concentrations the mechanism breaks down because reaction (2) then produces active as well as inert radicals, so that the "peninsula" opens and explosion is obtained at temperatures below the temperature of about 80°C at the tip of the peninsula.

For butane,  $C_4H_{10}$ , and higher hydrocarbons the explosion mechanism is analogous; however, the activation energies are lower. Accordingly, the peninsula broadens and shifts to the left, with the result that explosion is obtained already at very low temperatures. In addition, the chain-branching reaction (a) produces radicals  $R'$  ( $C_2H_5$  for butane and additional radicals  $R''$ ,  $R''' \dots$  for higher hydrocarbons) that undergo "satellite" branching and breaking reactions with rate coefficients  $k_1'$ ,  $k_2'$ ,  $k_a'$ ,  $k_b'$ , etc. This produces multiple explosion limits and induction periods as shown by the experimental curves of induction periods for butane-oxygen systems in Figure 3. The theory of the effect is illustrated in Figure 4 by a calculation showing two explosion regimes for the case of one satellite mechanism, using assumed values of the dimensionless ratios  $x = k_1 k_a / k_2 k_b$ ,  $y = (k_a / k_b) ([F_2] / [O_2])$  and the corresponding ratios  $x'$  and  $y'$ , and calculating the dimensionless induction period  $k_2 [F_2] \tau$ . The actual situation is further complicated by the chemistry of the reaction sequence following reactions (2), (2'), etc., which at high fluorine concentrations tends to obliterate the chain-breaking effect of these reactions.

Whereas the condition  $\alpha - \beta > 0$  depends only on the temperature and the ratio of the concentration of  $F_2$  and  $O_2$ , the development of the explosive reaction also requires a minimum absolute concentration of  $F_2$  for generating the temperature and free-radical concentration required for take-off of the main fuel-oxygen reaction. This occurs already with  $F_2$  concentrations of the order of one percent of the total molecular concentration. Above about 300°C a non-fluorine chain-branching mechanism via peroxidic free radicals  $ROO$  enters into the process of heat release and free-radical generation, and above about 1000°C chain branching occurs via  $OH$  radicals and  $H_2$  that are generated chiefly by decomposition of  $ROO$  and largely react according to  $H_2 + OH = H_2O + H$ ,  $H + O_2 = OH + O$ ,  $O + H_2 = OH + H$ . This provides a continuously accelerating run through the fluorine reaction to final combustion.

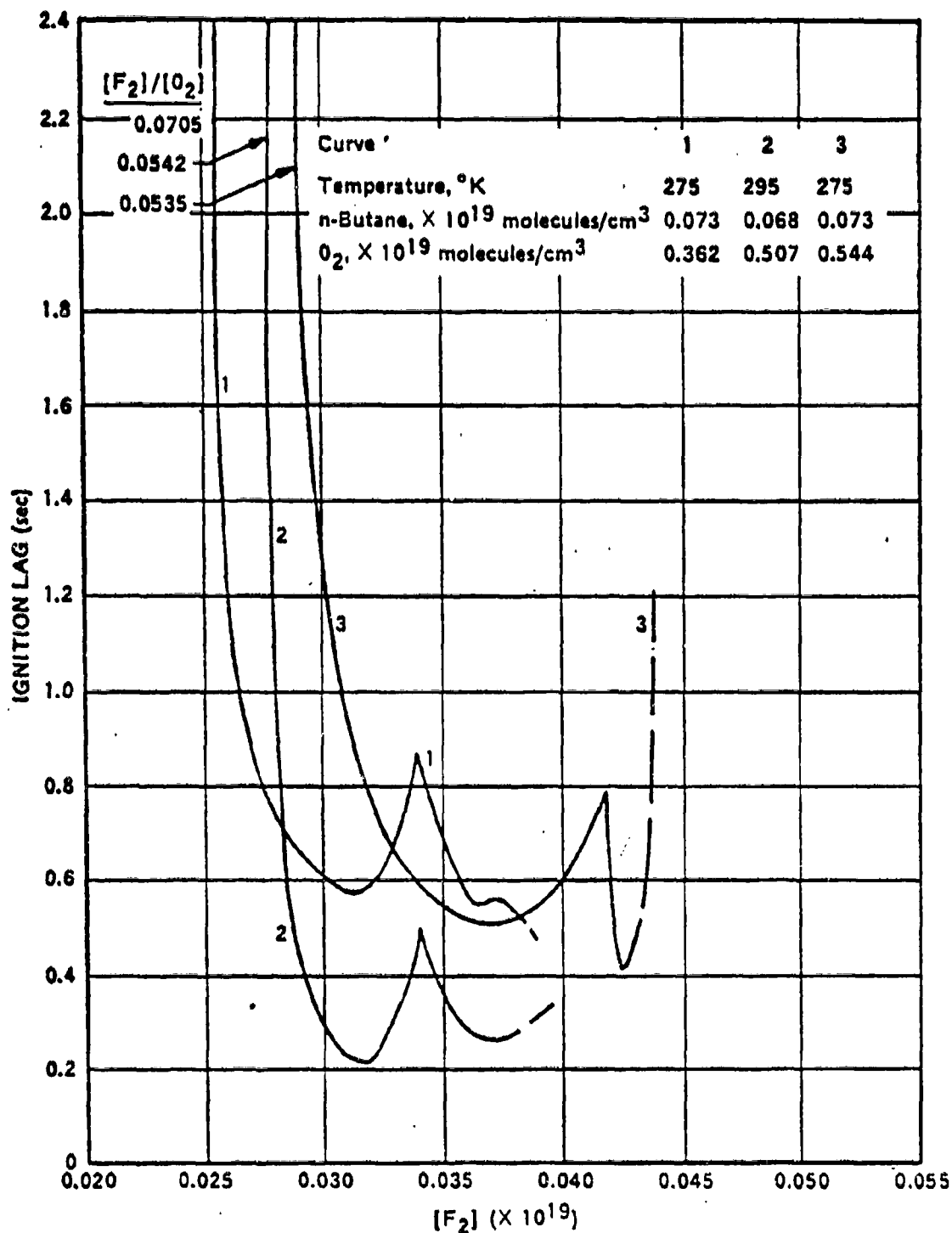


Figure 3. Ignition Lags of n-Butane/ $O_2$ / $F_2$ -Mixtures versus  $F_2$ -Concentration (Ref. 1). Experimental Procedure as in Figure 1.



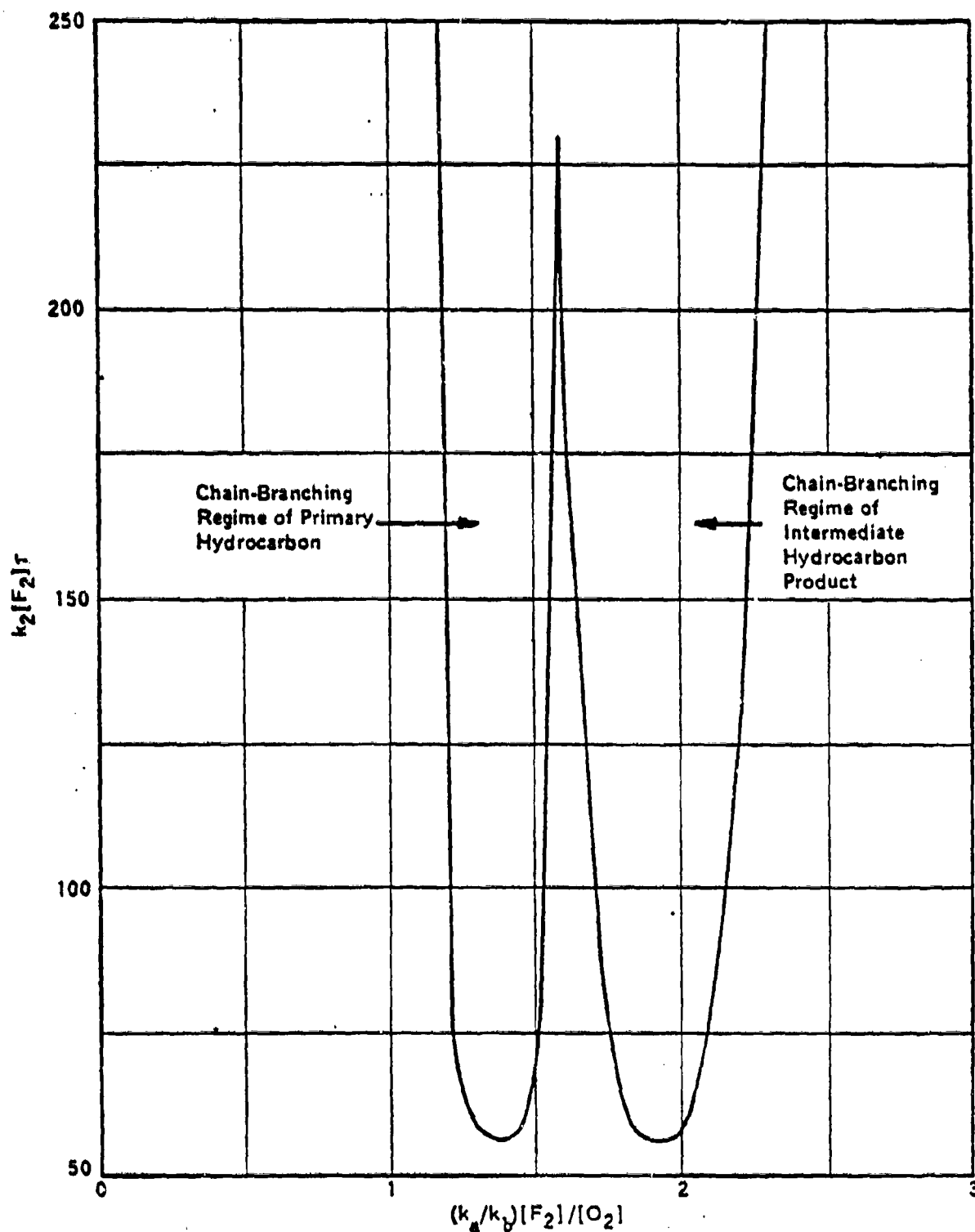


Figure 4. Sample Calculation Illustrating the Effect of an Intermediate Hydrocarbon Reaction Product on the Induction Period of Hydrocarbon- $O_2$ - $F_2$ -Explosions. (Ref. 1)

LIQUID FUELS WITH FLUORINE, CHLORINE TRIFLUORIDE (CTF) AND  
BROMINE TRIFLUORIDE (BTF) 2/

$F_2$  does not ignite droplet dispersions of liquid fuels in air even in large concentration, evidently because the reaction sequence  $R+O_2 \rightarrow ROO$  and  $ROO+F_2 \rightarrow 3R$  is limited by diffusion of  $O_2$  to the droplets and chain breaking via  $R+F_2$  predominates. Such dispersions as well as gaseous hydrocarbons in a state of turbulent mixing with air (i.e., the large-scale turbulence field contains pockets of unmixed hydrocarbon) are readily ignited by  $ClF_3$  in vapor form or droplet dispersion. On the other hand,  $ClF_3$  does not ignite premixed flammable gaseous hydrocarbon-air mixtures even in large concentration. Taking butane,  $C_4H_{10}$ , for example, this is explained by chain branching in collisions of  $ClF_3$  with the radical  $C_4H_9$ , i.e.,  $C_4H_9 + ClF_3 = C_4H_7 + 2HF + Cl + F + \sim 15 \text{ kcal/mole}$  ( $C_4H_9 = CH_3 \cdot CH_2 \cdot \dot{C}H \cdot CH_2$ ,  $CH_3 \cdot CH \cdot \dot{C}H \cdot CH_3$ ,  $CH_3 \cdot CH_2 \cdot \dot{C}H \cdot \dot{C}H$ ) and no chain branching in collisions with the radical  $C_4H_9OO$ , i.e.,  $C_4H_9OO + ClF_3 \rightarrow C_4H_9 + \text{neutral molecules}$ . It is certain that at the high  $O_2$  - concentrations in flammable gaseous hydrocarbon-air mixtures  $ROO$  predominates over  $R$ , and chemical considerations suggest that the reaction of  $ROO$  with either  $F_2$  or  $ClF_3$  produces a molecule  $HF$  and breaks the peroxidic bond  $O-O$ . With  $F_2$  the process thus generates two new free radicals, whereas with  $ClF_3$  the molecular fragments apparently combine with two of the available atoms, i.e.,  $Cl$  and  $F$ , to form neutral molecules. If  $ClF_3$  were substituted for  $ClF_3$  there would be two left-over atoms. This suggests that the pentafluoride  $ClF_5$  undergoes chain branching with both  $R$  and  $ROO$ , but this has not been experimentally verified.

With fuel droplet dispersions and  $ClF_3$  the induction period is extremely short and difficult to observe, reflecting a large  $\alpha$  - factor of the  $R + ClF_3$  reaction and the virtual absence of chain-breaking reactions, i.e.,  $\beta = 0$ . There is probably also a high rate  $n_0$  of spontaneous free-radical generation which may occur, for example, by the exothermic reaction  $C_4H_{10} + ClF_3 = C_4H_8 + 2HF + Cl + F$ .

With  $BrF_3$  the corresponding chain-initiating and chain-branching reactions are endothermic by about 4 kcal/mole. Accordingly, with this agent induction periods of millisecond order have been observed, which seems to exceed the induction periods for CTF by at least an order of magnitude.

#### OTHER AGENTS

At the recent AFOSR meeting M. Gerstein suggested numerous candidate agents that may be grouped into metal alkylates such as triethyl aluminum (TEA); volatile hydrides such as silanes, boranes and phosphines; peroxides; and compounds such as halogen nitrides which can be prepared in solution and decompose explosively in the free state. The methyl alkylates and the volatile hydrides offer the attractive feature of being inert to the fuel and reacting only with the air that is being entrained by the FAE cloud, which may possibly allow more time for the process of cloud generation and thus facilitate the realization of a chemical SWACER effect as discussed by Lee et al. However, the efficacy of these agents for FAE cloud initiation remains to be determined in laboratory experiments, bearing in mind subtleties of chemical kinetics and factors such as agent solubility in liquid hydrocarbon, which has been pointed out by Gerstein. In particular, chemical considerations suggest that the reaction of oxygen with the various hydrides may be inhibited by hydrocarbon vapors. Peroxides that are reasonably stable to be manageable do not offer the required  $\alpha$ -factor that would make these compounds effective free-radical donors at low temperature, and compounds such as the halogen nitrides are very sensitive to shock but are not known to ignite organic materials. There are nevertheless numerous chemical options, particularly with respect to metal organics and volatile hydrides, that invite laboratory studies.

#### CONCEPT OF FAE RESEARCH USING LIQUID FUELS

It seems to be generally agreed that liquid fuels should be used in practical FAE systems. If so, the options for the agent are at present restricted to the halogen fluorides, inasmuch as the existing experience does not offer alternative agents and the outlook of finding such agents is rather uncertain. The incendivity of the fluoride agents has been demonstrated, but it is a question how these agents should be used for blast generation in connection with the process of fuel dispersal in open air. The theory of the SWACER effect by Lee and coworkers provides answers in principle, but the means of realizing the effect remain to be determined.

For an initial approach to the problem of high-order blast generation, a procedure is being developed at Atlantic Research to generate a cloud of approximately 1 m average radius in a time of the order of 1 millisecond. By dispersing CTF with the fuel it should be possible to obtain a rate of combustion substantially equal to the rate of air entrainment which is characterized by the rate of advance of the serrated cloud boundary. It should thus be possible to generate a piston force that produces a shock-wave comparable to the detonation wave in a premixed cloud. This is analogous to shock initiation of a detonation wave in a premixed fuel-air system and thus constitutes an alternative approach that by-passes the concept of a gradient of induction periods which has been developed by Lee and coworkers. However, as experience with practical system configurations accumulates it may become possible to develop an explosive train which incorporates the feature of an energy release gradient in the cloud to produce shock wave amplification. The subject has already been considered previously in Ref. 2. An explosive train is proposed which generates a shock wave in the rear of the strongly driven cloud, and the cloud is pre-sensitized by dispersal of a comparatively slow-acting fluoride-base agent, so that the sensitivity to shock is increased and transition to detonation occurs at comparatively low strength of the primary shock.

At the recent AFOSR meeting a preliminary test has been reported which was designed to demonstrate that the fast-acting CTF can in fact be dispersed in a fuel such as Diesel oil by means of a high-explosive. This effect had not been obtained in previous laboratory experiments. The test was performed with a rather low-power cloud drive obtained from a small quantity of high explosive and the CTF-fuel reaction. By repeating the test in a nitrogen atmosphere it was found that the energy of the cloud drive was entirely absorbed by the fuel dispersal. Hence, the blast wave that was monitored in the open-air test was a FAE effect, generated only by air entrainment and combustion.

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